Effect of metal clusters on the swelling of gold–fluorocarbon–polymer composite films.

Annalisa Convertino
Istituto di Chimica dei Materiali C.N.R.– Area della Ricerca di Roma,
via Salaria Km 29.300, I–00016 Monterotondo St. Roma, Italy.

Antonio Valentini, Anna Bassi
Istituto Nazionale di Fisica della Materia – Dipartimento di Fisica – Università di Bari,
via Amendola 173, I–70126 Bari, Italy.

Nicola Cioffi, Luisa Torsi
Dipartimento di Chimica–Università di Bari,
via Amendola 173, I–70126 Bari, Italy.

Emilio N.M. Cirillo
Dipartimento Me. Mo. Mat.,
Università di Roma "La Sapienza,"
via A. Scarpa 16, I–00161 Roma, Italy.
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We have investigated the phenomenon of swelling due to acetone diffusion in fluorocarbon polymer films doped with different gold concentrations below the percolation threshold. The presence of the gold clusters in the polymer is shown to improve the mixing between the fluorocarbon polymer and the acetone, which is not a good solvent for this kind of polymers. In order to explain the experimental results the stoichiometry and the morphology of the polymer–metal system have been studied and a modified version of the Flory–Huggins model has been developed.

Polymers can be combined with inorganic materials to form hybrid polymer–inorganic structures with a rich variety of physical and chemical properties. They offer a powerful tool to design novel devices which take advantage of the immense tailorability and the low cost processing of polymers. Stacks of alternating layers of polymer and oxide have been recently used as high reflectivity dielectric mirrors [1–3], emitting polymers are sandwiched between reflecting inorganic electrodes in order to realize organic LED devices [4, 5], inorganic–polymer composite films consisting of inorganic nanoparticles (i.e. metal, oxide or semiconductor clusters) dispersed in a polymeric matrix are commonly employed as sensors [6, 7] and more recently have been found applications in the fabrication of all–polymer mirror for the development of all–organic optoelectronics devices [9, 12].

We study, here, the absorbing behavior of an hybrid polymer–inorganic structure plunged into a liquid solvent (see [13–16]). When a polymer is exposed to a liquid solvent, the liquid enters the polymer and diffuses inside holes and microvoids in its structure. The polymer swells to an equilibrium state where the tendency to absorb solvent molecules is balanced by the elastic response of the network. The *degree of swelling*, namely the volume fraction of polymer in the mixture at equilibrium, has been calculated in pioneering papers [17] by means of thermodynamics arguments (see, also, [18]). Many important steps have been recently done toward the understanding of both the equilibrium (see the recent review [13]) and non–equilibrium (see, for instance, [19–23]) properties of swelled polymers. Nevertheless, in spite of the rapidly expanding interest for pure polymer and hybrid polymer–inorganic structures, due to the complexity of the swelling phenomena, a complete theory and a full understanding of the fundamental physics of swelling are still lacking.

In this letter we study the swelling behavior in a particular inorganic–polymer system: the gold–fluorocarbon–polymer composite with a metal content below the percolation threshold. This system consists of small gold clusters, with mean diameter ranging from $2nm$ up to $10nm$ (controlled by the doping), embedded in the fluorocarbon matrix [24, 25]. Then, we show how the presence of metal clusters can improve the absorbing power of the fluorocarbon polymer when it is exposed at the vapors of acetone, which is known to be a poor solvent for fluorinated polymers. Moreover we propose a genuine entropic interpretation of this effect based on a variation on the theme of the Flory–Huggins model [17, 18].

Samples of gold–fluorcarbon, with typical thickness of about $100nm$, have been deposited at room temperature on quartz substrate by ion beam sputtering. The films have been obtained by cosputtering Teflon and gold targets with Ar^+ ion beams. The Au content φ, namely the gold volume fraction in the film, has been varied in the interval $0 \leq \varphi \leq 0.18$, i.e. below the percolation threshold which has been found in these materials to be $\varphi_c \simeq 0.37$ [24]. More details on the synthesis of these systems are reported in [8, 9]. Transmission Electron Microscopy (TEM) has been employed to assess the morphology of the composite films. Samples for TEM characterization have been deposited on 400 mesh Formwar-coated nickel grids up to a thickness of $10nm$, in order to be transparent enough to the electron

beam. Film surface composition has been studied by means of X–ray Photoelectron Spectroscopy (XPS) by using a Leybold LHS10 spectrometer equipped with an unmonochromatised AlKα source. Calibration of the spectra has been performed by taking the CF_2 component of the C1s electron peak (Binding Energy = 291.6eV) as internal reference [10]. Curve-fitting has been performed as reported in reference [11]

In Fig. 1 high and low magnification TEM photographs of the composite film with $\varphi = 0.15$ are reported. As it is evident from the figure, the composite film shows a high uniformity and the gold clusters are equally distributed in all the material. This allows to exclude the presence in the films of large area pores/holes, which did not be expected in films deposited by means of sputtering technique. Indeed, the high kinetic energy of the sputtered species produces very dense films. The clusters of the sample in Fig. 1 are characterized by an average diameter of $3.6 \pm 1.5nm$, typical value for this kind of materials [24, 25].

A quantitative surface chemical analysis of the films has been achieved by XPS. Fig. 2 reports a typical high resolution C1s region for gold–fluorocarbon film ($\varphi = 0.15$ in the present case). The spectrum clearly indicates the presence of different carbon chemical environments. Six different peaks have been used to fit the signal. Their attribution is reported in Tab. 1, along with their abundance. The CF_3, CF_2, CF, C–CF, C–C in a fluorinated environment species are typical of a fluorocarbon matrix [8, 26]. The peak falling at $288.5 \pm 0.2eV$ can be simultaneously attributed to carbonyl (C=O) or fluorinated-unsaturated groups (C=CF) [27]. C=O groups are minor species that are commonly present in this kind of sample, that has been exposed to air before ex-situ XPS characterization. However, the oxygen surface percentage was extremely low in all the samples (always less than 1%), and this value is too low as compared to the relatively high intensity of the C1s component falling at 288.5eV, that should be stoichiometrically balanced by an atomic oxygen percentage of at least $3 - 4\%$. Consequently, C=CF species are expected to contribute to this signal. Their presence is confirmed by the weak shoulder (not fitted) centered at approximately 296eV and due to shake-up phenomena that are typical of unsaturated carbons [27]. It is worth noting that the C1s component falling at the lowest binding energy also has a contribution due to hydrocarbon contaminants deriving from the vacuum system. Quantitative treatment of the fitting data has been carried out following two opposite hypotheses: *(i)* the peak is exclusively due to contaminants, *(ii)* the peak is exclusively due to not-fluorinated branched carbons of the organic film. The results obtained accordingly have been then averaged. It is important to note that the metal depositions in/onto fluorocarbon materials are known [10] to cause fluorine losses from the polymer, thus promoting rearrangements and cross–linking processes. The areas of peaks relevant to tertiary and quaternary carbon species (CF, C–CF and, eventually, C–C in a fluorinated environment) can be used to quantify the cross-linking extent (expressed as the percentage of branched carbons). The results are reported in Tab. 2, where Ψ_1 is the percentage of branched C and Δ_1 is the ratio between the branched C percentage and that at $\varphi = 0$ in the hypothesis *(i)*, whereas Ψ_2 and Δ_2 are the same quantities calculated in the hypothesis *(ii)*. In the present case the abundance of these components increases significantly upon gold inclusion and the amount of branched carbons almost doubled itself in the $\varphi = 0.18$ composition.

It has been remarked, see [7, 21], that in the inorganic–polymer composites above the percolation threshold the absorption power abruptly decreases. Here we consider different films, with different metal content below the percolation threshold, and we measure the equilibrium concentration of acetone in the swelled film as a function of the vapor pressure. We describe, now, our swelling experiments: the films have been inserted in a vacuum chamber, characterized by a base pressure approximately equal to $1 \times 10^{-3}mbarr$, where acetone vapors have been introduced. The pressure P of the acetone vapors in the vacuum chamber has been measured by a Pirani gauge. The swelling of the film produces a relative thickness variation Δt, that has been monitored by an ellipsometer operating at the single wavelength of $632.8nm$. In the range of the acetone vapor pressure analyzed we did not observe any change in the refractive index for the sample with $\varphi = 0$. Then this allows us to express the volume fraction y of solvent in the mixture as the equality $y = \Delta t/(t + \Delta t)$ and to obtain y as a function of the relative pressure P/P_0 (where $P_0 = 242mbarr$ is the saturation vapor pressure of the pure acetone at room temperature [29]) by only measuring the thickness variations. In Fig. 3 our results have been plotted for different Au contents, namely $\varphi = 0$ (●), 0.05 (■), 0.13 (▲), 0.18 (▼) (the solid lines are only guides for eyes). The sample with $\varphi = 0$ shows a very low absorbing power, which saturates at $P/P_0 \leq 0.05$. This behavior confirms the low solubility of the fluorocarbon polymer in acetone. From Fig. 3 it is evident that the swelling effect is enhanced by the presence of the gold clusters in the polymer, indeed at fixed values of P/P_0 the volume fraction of solvent y increases with the Au content.

This effect is rather surprising because the presence of the metal should reduce the volume effectively occupied by the polymer in the sample and inhibit the absorption. Moreover the XPS measurements indicate that the inclusion of metal clusters increases the cross-linking in the films, which become more rigid and less soluble [17], and the TEM results exclude the presence of holes and pores in our films. This phenomenon looks definitely interesting both from the point of view of the applications and from that of the understanding of the fundamental physics of swelling. Indeed, it suggests that the presence of topological defects in the polymer matrix, such as our non–percolating golden obstacles, favors the absorption phenomenon. We will try to explain our results via an entropy based argument.

The equilibrium concentration y of solvent in the mixture is the solution of the equation:

$$RT \log \frac{P}{P_0} = \frac{\partial}{\partial n} \Delta G(y) \quad , \tag{1}$$

where R is the gas constant, T is the temperature, P_0 is the saturation vapor pressure of the pure solvent, n is the number of moles of solvent in the mixture and $\Delta G(y)$ is the free energy of mixing. The left–hand side is nothing but the difference between the chemical potential of the pure solvent in the vapor and liquid phase, whereas the right–hand term is the difference between the chemical potential of the solvent in the mixture and in the pure liquid phase. Flory–Huggins (see [17, 18]) derives the expression of the derivative of the free energy of mixing $\partial \Delta G^{\mathrm{pure}}(y)/\partial n = RT \left\{ \alpha w^2 + \log y + w + \beta \left[w^{1/3} - w/2 \right] \right\}$ where $w = 1 - y$ is the volume fraction of polymer in the mixture, the *degree of swelling*, and α, β are dimensionless positive constants respectively related to the heat of dilution and to the effect of the cross–links. For a suitable choice of the parameters α and β, the above function increases monotonically from $-\infty$ to 0 when $0 \leq y \leq 1$. Hence, the polymer absorbs solvent until y is so large that equation (1) is satisfied.

The fact that the chemical potential of the solvent in the mixture increases with y can be understood through an heuristic argument: the free energy of mixing can be written as $\Delta G = \Delta H - T \Delta S$, where ΔH and ΔS are respectively the enthalpy and the entropy of mixing. Now, $\partial \Delta S / \partial n$ is surely positive, but decreasing with y. Indeed, when more solvent is added to the mixture its entropy increases, but this increment is smaller when y is larger.

In the case of a inorganic–polymer composite it is natural to suppose that the entropy of mixing is more sensitive to the absorption of solvent. So we can conjecture that $\partial \Delta S^{\mathrm{pure}}/\partial n \ll \partial \Delta S^{\mathrm{comp}}/\partial n$: this implies that the chemical potential is smaller in the case of composite materials, so the equilibrium (1) is reached for larger values of y. A modified version of the lattice Flory–Huggins model leads to $\partial \Delta G^{\mathrm{comp}}(y)\partial n = \partial \Delta G^{\mathrm{pure}}(y)\partial n - \lambda \varphi w^2/(1 - \lambda \varphi w)$, where $w = (1 - y)(1 - \varphi)$ is the degree of swelling, λ is a dimensionless positive constant and the new term $-\lambda \varphi w^2/(1 - \lambda \varphi w)$ is the entropic correction conjectured above. In Fig. 4 our data have been fitted with the parameters $\alpha = 0.8$, $\beta = 0.1 \times (\Delta_1 + \Delta_2)/2$ and $\lambda = 6$. The low pressure ($P/P_0 \leq 0.05$) experimental data are quite well reproduced by equation (1) with the corrected chemical potential and φ assuming the measured values $\varphi = 0, 0.05, 0.13, 0.18$. It is important to remark that in the four graphs in Fig. 4 the parameters α and λ are kept fixed, and only the parameter β and φ are varied; this suggests that the effect is mainly entropic.

At $P/P_0 = 0.05$ the trend of the experimental data changes abruptly, as a consequence of the insolubility of the fluorocarbon polymer matrix in acetone, indeed at $\varphi = 0$ a saturation solvent concentration is approached. Flory–Huggins models cannot describe the saturation regime, but as φ increases the composite films become more and more soluble and the agreement between experimental data a theoretical predictions is improved. Although this agreement is reasonably good at $\varphi \neq 0$, it is clear that different swelling mechanism should be taken into account. A possible explanation could be the electric and chemical interaction between acetone molecules and the gold clusters.

Finally, we briefly describe our modified Flory–Huggins lattice model: a three–dimensional cubic lattice with N sites is filled with N_w polymer chains, each chain is made of κ monomers and each monomer occupies a lattice site; the remaining $N - \kappa N_w$ sites are occupied by $N_y = N - \kappa N_w$ molecules of solvent. The support of each chain is a sequence of κ pairwise nearest neighboring sites. The effect of the doping is introduced by supposing that some of the bonds on the lattice are broken, in the sense that two neighboring monomers of a chain cannot occupy two neighboring sites of the lattice sharing a broken bond. The density of broken bonds is chosen equal to $\lambda \kappa N_w \varphi / N$ where λ is a positive constant. The configurational entropy is then computed as the Boltzmann constant times the logarithm of the number of possible configurations of the system. By deriving the entropy of mixing with respect to N_y we obtain our entropic correction term.

We conclude that in gold–fluorocarbon–polymer composite films with metal content below the percolation threshold the swelling phenomenon is enhanced by the presence of inorganic clusters in the polymer. These results suggest that in the swelling of hybrid inorganic–organic materials, like inorganic–polymer composites, the inorganic component plays an important role in the swelling of the polymeric part so that a rather extensive territory could still be explored if different inorganic particles and matrix polymers were considered. This could improve the understanding of an important phenomenon involving organic matter and would also offer a powerful tool in the design and in the fabrication of polymer devices employing the swelling.

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[1] A. Convertino, A. Valentini, T. Ligonzo, R. Cingolani, *Appl. Phys. Lett.* **71** (6), 732 (1997).
[2] Y. Fink et al., *Science* **282**, 1679 (1998).
[3] M. De Vittorio et al., *Superlattices and Microstructures* **25** (1/2), (1999).
[4] M. Hiramoto, J. Tani, M. Yokayama, *Appl. Phys. Lett.* **62**, 666 (1993).
[5] N. Takada, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **63**, 2032 (1993).
[6] G.G. Neuburger and P.C. Warren, *Sensors and Actuators* **B1**, 326 (1990).
[7] C. Brosseau et al., *J. Appl. Phys.* **81** (2), 882 (1997).
[8] F. Quaranta, A. Valentini, P. Favia, R. Lamendola and R. d'Agostino *Appl. Phys. Lett.* **63** (1), 10 (1993).
[9] A. Convertino, A. Valentini, R. Cingolani, *Appl. Phys. Lett.* **75** (3), 732 (1999).
[10] M.K. Shi, B. Lamontagne, A. Selmani, L. Martinu, E. Sacher, M.R. Wertheimer and A. Yelon, *J. Vac. Technol. A* **12** (3), 807 (1994)
[11] C. Malitesta, I. Losito, L. Sabbatini and P.G. Zambonin, *J. Elec. Spec. and Rel. Phen.* **76**, 629 (1995).
[12] P.K.H. Ho, D.S. Thomas, R.H. Friend, N. Tessler, *Science* **25**, 233 (1999).
[13] F.A. Escobedo, J.J. de Pablo, *Physics Reports* **318**, 85–112 (1999).
[14] R. Dagani, *Chem. Eng. News*, p. 26 (9 June 1997).
[15] F.J. Doyle, C. Dorski, J.E. Harting, N.A. Peppas, *Control and modeling of drug delivery devices for the treatment of diabetes. Proceeding of the 1995 American Control Conference, 1995*, 6 vol. LXXII + 4483 pp. 776–80.
[16] F.J. Doyle, Responsive Gels: Volume Transitions, Vols. I and II, in Advences in Polymer Sciences 109–110, Edited by K. Dusek, Springer, Berlin, 1993.
[17] P.J. Flory, *J. Chem. Phys.* **10**, 51 (1942); M.L. Huggins, *J. Chem. Phys.* **46**, 151 (1942); P.J. Flory, R. Rehner, *J. Chem. Phys.* **11**, 521 (1943).
[18] P.J. Flory, *Principles of Polymer Chemistry* (Cornell Uni. Press, Ithaca, 1953); L.R.G. Treolar, *The Physics of Rubber Elasticity*, (Oxford Uni. Press, Oxford 1975); R.J. Young, P.A. Lovell, *Introduction to Polymers*, (Chapman & Hall, London 1981).
[19] G. Rossi, K.A. Mazich, *Phys. Rev. A* **44**, R4793 (1991).
[20] G. Rossi, K.A. Mazich, *Phys. Rev. E* **48**, 1182 (1993).
[21] K. Miyasaka et al., *J. Mater. Sci.* **17**, 1610 (1982).
[22] M.C. Lee, N.A. Peppas, *J. Appl. Polym. Sci.* **47**, 1349 (1993).
[23] T. Tanaka et al., *Nature* **325**, 796 (1987),
T. Tanaka et al., *Phys. Rev. Lett.* **45**(20), 1636 (1980)
[24] J. Perrin, B. Despax, E. Kay, *Phys. Rev. B* **32**, 719 (1985).
[25] A. Nannini, P.E. Bagnoli, A. Diligenti, B. Neri, S. Pugliese, *J. Appl. Phys.* **62**, 2138 (1987).
[26] R. D'Agostino, F. Cramarossa, F. Fracassi, E. Desimoni, L. Sabbatini, P.G. Zambonin and G. Caporiccio, *Thin Solid Films* **143**, 163 (1986).
[27] A. Dilks, in *Electron Spectroscopy, Theory, Techniques and Applications*, volume 4, (C.R. Brundle and A.D. Baker Ed.s, Academic Press, New York 1981).
[28] Y. Yagil, P. Gadenne, C. Julien, G. Deutscher, *Phys. Rev. B* **46**, 11342 (1991).
[29] J.A. Riddick, W.B. Bunger, *Techniques of Chemistry* (Wiley–Interscience, 1970)
[30] B. Abeles, *Appl. Solid State Sci.* **6**, 1 (1976).

Figure Captions

Fig. 1: TEM photographs relevant to a gold–fluorocarbon film having a gold volumetric fraction $\varphi = 0.15$ and a thickness of $10 nm$. The gold cores mean diameter was $3.6 \pm 1.5 nm$.

Fig. 2: High resolution C1s XPS spectrum and curve–fit results relevant to gold–fluorocarbon film $\varphi = 0.15$.

Fig. 3: The volume fraction of solvent in the mixture as a function of the relative pressure P/P_0 at different Au contents: $\varphi = 0$ (●), 0.05 (■), 0.13 (▲), 0.18 (▼) (the solid lines are only guides for eyes).

Fig. 4: Comparison between experimental data and theoretical results (solid lines) for the volume fraction of solvent in the mixture at different Au contents: a) $\varphi = 0$;, b) $\varphi = 0.05$; c) $\varphi = 0.13$; d) $\varphi = 0.18$.

Tables

	CF_3	CF_2	CF	$C = O$ and $C = CF$	$C\text{–}CF$	$C\text{–}C$
Binding energy (eV)	293.7 ± 0.1	291.8 ± 0.1	289.8 ± 0.1	288.5 ± 0.2	286.9 ± 0.3	285.2 ± 0.3
%	10.6 ± 0.3	43.2 ± 0.3	16.5 ± 0.7	9.4 ± 0.7	12.8 ± 0.5	7.4 ± 0.4

Tab. 1: Peak attributions and quantitative data to the fitting reported in Fig. 2.

	$\varphi = 0$	$\varphi = 0.05$	$\varphi = 0.13$	$\varphi = 0.18$
Ψ_1	16.0	25.0	30.1	31.6
Δ_1	1	1.6	1.9	2
Ψ_2	16.6	27.4	34.8	37.3
Δ_2	1	1.6	2.1	2.2
$(\Delta_1 + \Delta_2)/2$	1	1.6	2.0	2.1

Tab. 2: Estimations of the cross–linking extent upon varying the gold content in the composite films. Ψ_1 is the percentage of branched C and Δ_1 is the ratio between the branched C percentage and that at $\varphi = 0$ in the hypothesis *(i)*, whereas Ψ_2 and Δ_2 are the same quantities calculated in the hypothesis *(ii)*.
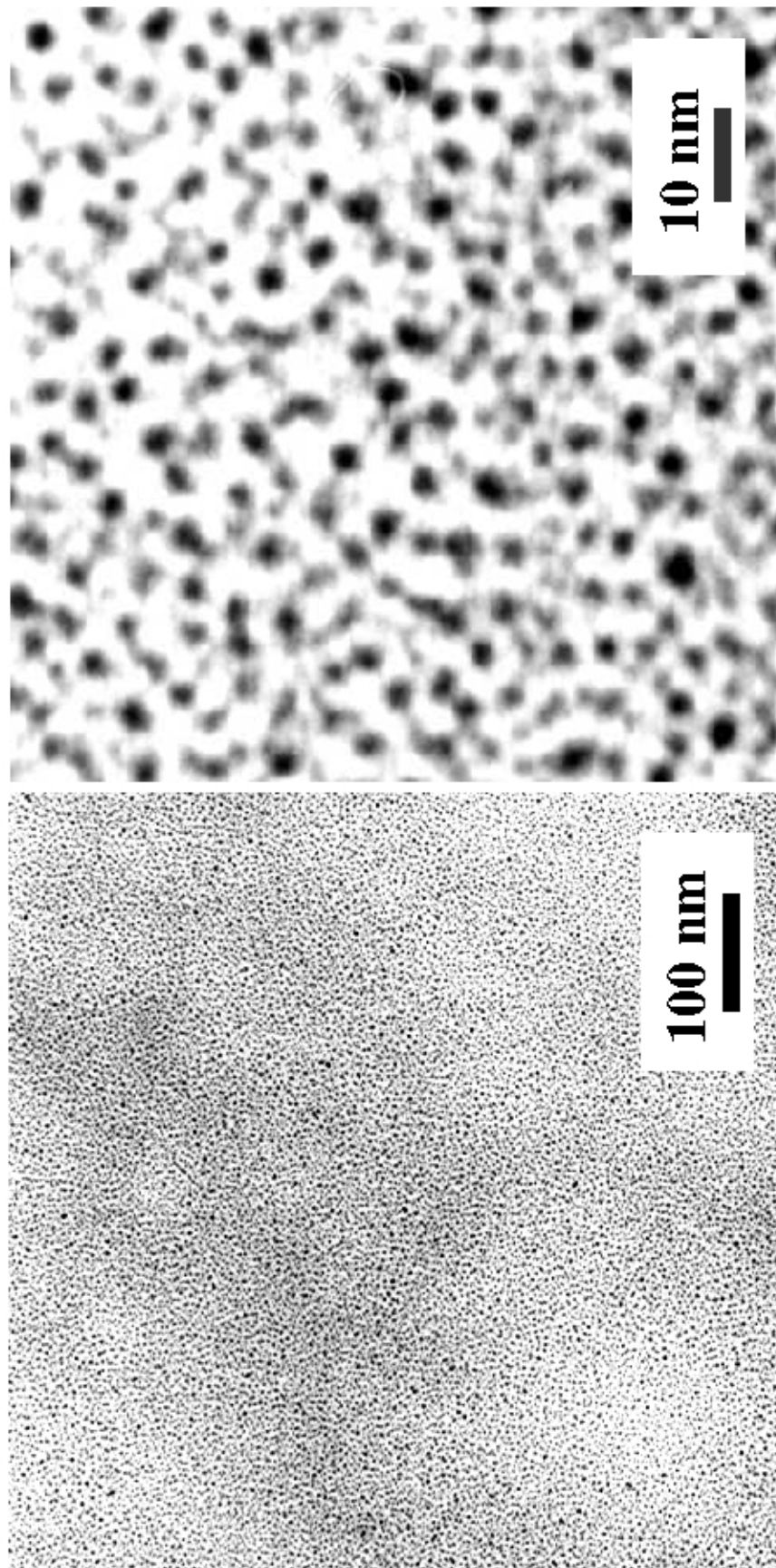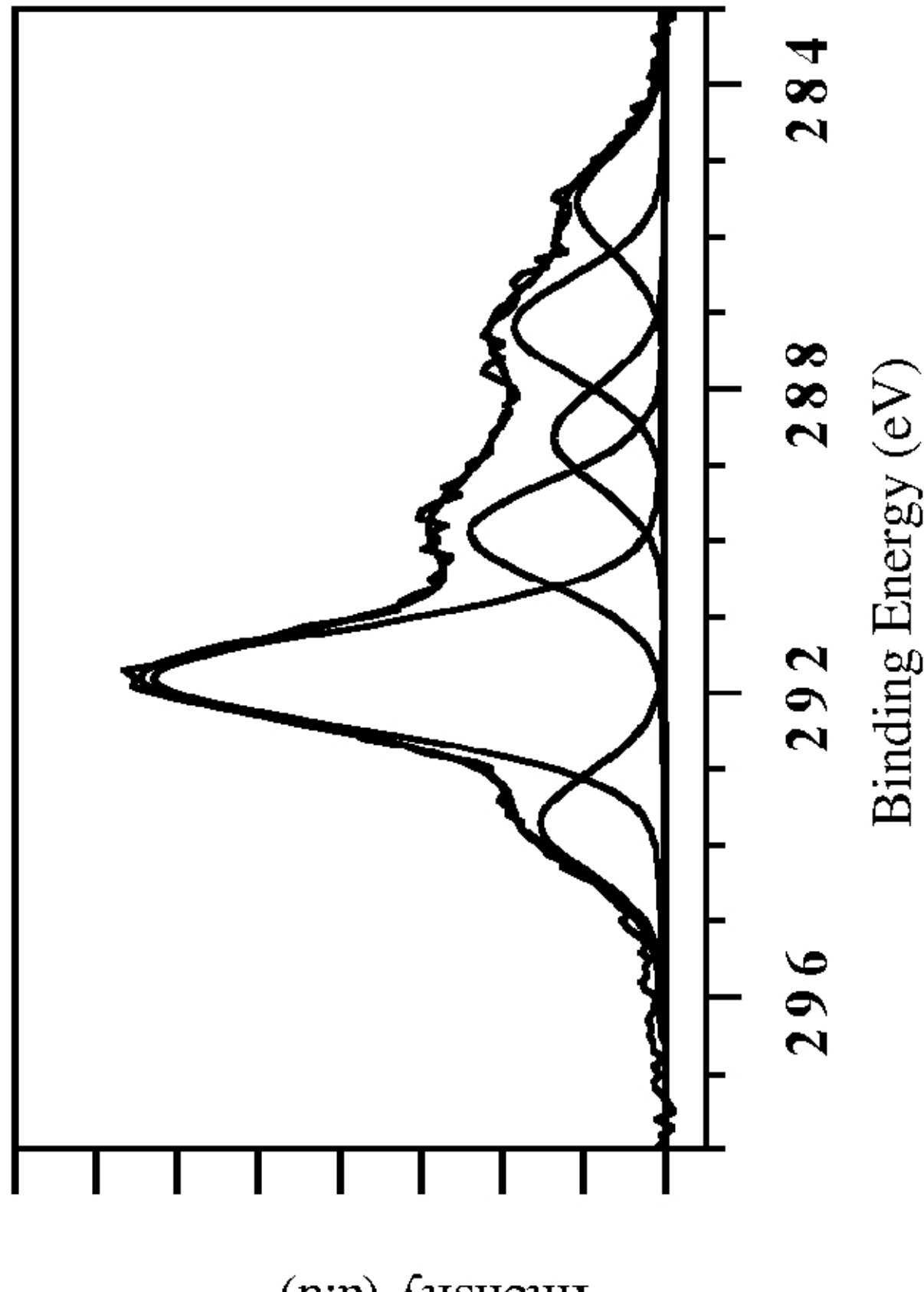
Fig.1

Fig.2

Binding Energy (eV)